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Vapor Sensing Properties of a Conductive Polymer Composite Containing Nickel Particles with Nano-scale Surface Features*

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Abstract— This paper presents an unusual conductive polymer composite, produced by Peratech Ltd under the trademark QTC™, which has many vapor sensing applications. Nickel particles are intimately coated by an elastomeric binder such that no percolative conduction can occur. However, the nickel particles are shown to possess spiky nano-scale surface features, which promote conduction by a field assisted quantum tunneling mechanism. Granular QTC™ can be dispersed into a polymer matrix to produce a vapor sensor. Under exposure to a vapor, the polymer swells and resistance of the composite increases. In this work, granular sensors are subjected to acetone and tetrahydrofuran (THF) vapors. The response for THF shows an increase in resistance of a factor of 10^8 , over a time-scale of a few seconds. This response is larger and faster than many conventional vapor sensing composites. The response and subsequent recovery can be explained by a case II diffusion model, and linked to Hildebrand solubility parameters of the vapor and polymer components.

I. INTRODUCTION

Artificial olfaction has extensive applications in the detection of volatile organic compounds (VOCs). For example, such a sensor may be used in the detection of harmful vapors in the defense industry and the detection of vapors emitted from human skin for many healthcare applications [1, 2]. A conventional realization of such an ‘electronic nose’ is the dispersion of electrically conductive filler particles in an insulating polymer matrix. Under compression, filler particles are brought closer together and the conductivity increases according to the percolation theory. Conversely, exposure to a sufficient vapor concentration causes the polymer matrix to swell, and this produces a decrease in conductivity.

This paper presents a novel material produced by Peratech Ltd under the generic trademark QTC™, which is capable of producing a large response to a range of VOCs.

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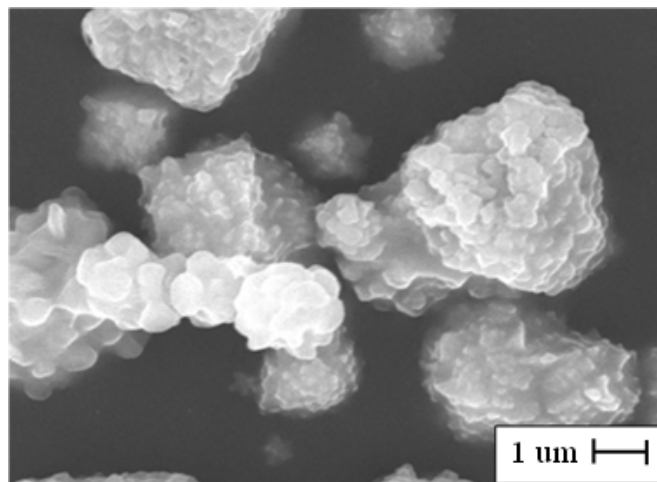


Figure 1. Nickel particles used in QTC™ materials. The particle has a spiky morphology, with clearly visible surface protrusions. These nano-scale features give the QTC material its unusual electrical properties. Charge is stored on the spiky tips, promoting conduction by field assisted (Fowler-Nordheim) quantum tunnelling.

Unlike other conventional composite materials, QTC™ in its granular form is capable of producing a very large electrical response over a short time scale, typically in the order of a few seconds. The granules are formed by a patented process, by mixing nickel particles into a silicone binder [3]. The nickel particles, typically 1 – 10 μm in size, show spiky nano-scale features on the particle surface, as shown in Fig.1. The spiky tips allow electrical conduction through a field-assisted quantum tunneling mechanism, such that the granules are capable of exhibiting great sensitivity to applied pressure – a property that can be utilized to great effect in vapor sensing devices.

The electrical response of granular QTC™ is investigated for high concentrations of both acetone and tetrahydrofuran (THF) vapors. Results are compared to previous work conducted by Graham *et al* [4, 5] and explained by consideration of the solubility parameter of the materials involved.

II. THEORY

A. Conduction Mechanisms and Vapor Sensing in Conductive Polymer Composites

Composites consisting of electrically conductive filler particles dispersed in an insulating matrix have been studied for over 60 years, where typical fillers include carbon black, expanded graphite and carbon nanotubes [6-8]. The filler

loading affects the intrinsic conductivity of the composite: for a loading at or above the percolation threshold the conductivity is seen to increase dramatically. This is primarily explained by percolation theory or effective medium models. Under exposure to a vapor, the polymer matrix may swell, increasing the distance between neighboring filler particles so that the electrical conductivity of the composite decreases. Swelling of the polymer is greatest when there is a match between the solubility parameter of the polymer and that of the vapor. Each element in an array of sensors can be designed to give an optimum response to an assortment of chemical vapors, thus producing an electronic nose. The typical response time is usually of the order of a few minutes. The largest responses are produced by operating the system close to the percolation threshold. However, near the percolation threshold, small changes in filler content result in large changes in electrical response so that it becomes difficult to produce reliable sensors capable of giving repeatable results.

QTC™ material consists of nickel particles fully wetted by a silicone elastomeric binder. Because the nickel particles are completely wetted by the polymer, even at loadings above the percolation threshold there is no direct contact between adjacent particles and the material has a very high resistance. However, upon any kind of mechanical deformation, the material has been shown to exhibit a very large decrease in resistance. For example, during compression the sample resistance can fall by a factor of $> 10^{14}$. It has also been shown that charge concentration at the tips of the spiky filler particles results in large electric fields, so that charge transport occurs through electric field assisted quantum tunneling rather than by direct contact between the particles [9, 10].

Granular QTC™ can be used to produce a vapor sensor which is capable of solving some of the issues highlighted above. The granules are mixed into an additional polymer matrix, which binds and compresses the granules so that as-made they are conductive. Under exposure to a vapor, the polymer swells and releases the pressure on the granules, causing an increase in resistivity.

B. Vapor Absorption in Polymers

The response a polymer experiences after exposure to a solvent vapor is governed by absorption thermodynamics and diffusion of the solvent into the polymer. Diffusion of the solvent vapor into the polymer results in mixing between the polymer and vapor molecules. This causes an increase in entropy of the system. However, the absorbed vapor molecules also cause dilation of the polymer. This reduces the number of possible orientations of the polymer chains. As the chains orientate to decrease their entanglement, the order of the system increases and thus the entropy decreases. In order for the vapor-polymer reaction to occur, the entropy decrease caused by polymer swelling must be overcome by the entropy increase caused by the vapor-polymer mixing process. Only then can more solvent be absorbed. If the polymer swelling contribution outweighs that of the mixing process, the reaction will not occur and no more vapor is absorbed.

The Hildebrand solubility parameter gives an indication of the relative solvation properties of a specific solvent [11]. For solution to occur, solvent molecules must overcome the inter-molecular forces present in the solute. This is more efficient when the contributions to the inter-molecular forces (both polar and dispersive) are of similar magnitude for the solvent and solute.

The compatibility of a polymer-solvent pair can be estimated by assessing

$$\sqrt{|\delta_s - \delta_p|} \leq 1, \quad (1)$$

where the subscripts s and p refer to the solvent and polymer respectively. For a value less than 1, the solvent will dissolve the polymer [12].

III. EXPERIMENTAL

A. Granular QTC™ Samples

QTC granules, consisting of nickel particles dispersed in a silicone binder, are made in-house at Peratech Ltd. The sensors used here were constructed for a previous investigation into the vapor sensing properties of granular sensors. The granules were mixed into a polyvinyl chloride (PVC) polymer and chlorobenzene solvent and dispersed onto substrates. Further details of their composition and manufacture can be found elsewhere [4].

B. Vapor Sensing Equipment

The equipment used to expose the granular sensors to VOC vapors is shown in Fig.2. Sensors were placed in a custom-made chamber which allowed the through-flow of vapor. The chamber was kept in an incubator at $20 \pm 1^\circ\text{C}$. A Keithley 2740 multimeter, connected to a PC via a GPIB card and running a custom LabView programme, was used to monitor the resistance across the sensors.

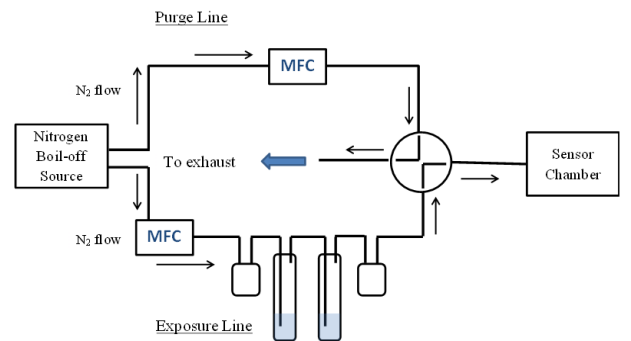


Figure 2. Vapor sensing test apparatus. Flow direction is represented by the arrows. To create the solvent vapor, nitrogen gas from a boil-off source passes through two bubble chambers containing the test solvent (with a liquid trap before and after to prevent liquid backflow through piping). This is the exposure line. A separate purge line contains pure nitrogen gas. Vapor flow into the sensor chamber is controlled by a manual four way switch. In the configuration shown, the sensor chamber is exposed to the test vapour whilst the nitrogen is diverted into an exhaust.

Two separate vapor lines were constructed with Teflon tubing. The purge line provided a flow of nitrogen from aliquid nitrogen boil-off source at a pressure of 2 bar. A Mass

Flow Controller (MFC) was installed to maintain the flow rate at 3 l/min. The vapor line consisted of a separate nitrogen flow leading into two bubble chambers in series, containing either acetone or THF. A liquid trap was placed either side of the bubblers to prevent any liquid entering the tubing. Flow into the bubblers was maintained with a Cole-Palmer digital MFC set to approximately 80 ml/min. This produced a nitrogen carrier gas saturated with the required test vapor.

The bubblers were immersed in a Grant LTC20-40RS oil bath filled with Baysilone M3 silicone fluid with temperature control accurate to 0.1°C. The temperature of the bubblers controlled the resulting vapor concentration.

Vapor flow over the sample was controlled by a manual four-way valve. In the purge configuration, pure nitrogen was allowed to pass over the sensor whilst the solvent vapor was diverted into an exhaust line. In the exposure configuration, the solvent vapor was passed over the sample whilst the pure nitrogen was diverted into the exhaust. In a typical experiment, the sensor was initially purged with nitrogen for 10 minutes. This was followed by a 1 minute exposure to vapor and a 9 minute nitrogen purge. This cycle was repeated up to 5 times.

IV. RESULTS

Fig.3a shows the response of the granular sensor to THF vapor over 5 purge-exposure cycles. Fig.3b shows a single exposure/purge cycle on an expanded time scale. From an oil bath temperature of 19.6°C, the partial pressure of the THF vapor was calculated to be 127 mmHg which corresponds to a concentration of 167 000 ppm.

Prior to the first exposure (at a time of 10 minutes) the initial resistance of the sensor is 860 Ω . At the onset of the THF exposure, the resistance increases over 8 orders of magnitude in the first 5 seconds, however the resistance is limited to 100 M Ω due to equipment limitations. This

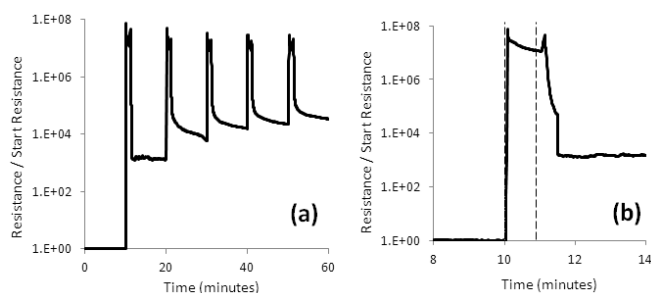


Figure 3. (a) The response of QTCTM granules dispersed in PVC polymer, after 5 exposures to THF vapor at a concentration of 167 000 ppm. During the first exposure, the resistance of the sensor increases by several orders of magnitude. After the exposure, recovery is much slower than the initial response and the resistance tends towards a baseline much higher than the start resistance. (b) The first exposure/purge cycle is plotted on an expanded time scale. The dashed lines indicate the exposure period.

response has been observed in granular sensors previously [4, 5], and is due to vapor absorption into the polymer matrix, causing the polymer to swell. This reduces the compression

on the enclosed granules, so the enclosed nickel particles move further apart and therefore the resistance increases. During the purge process, the resistance drops again but does not reach the start value. The rate of recovery is much slower than the rate of response, and this becomes more pronounced after the second exposure. Graham attributes this to a case II diffusion mechanism [4], where in the response regime a wavefront of vapor propagates through the polymer, driving the vapor into the polymer through a concentration gradient. In the purge mechanism there is no wavefront, so the vapor molecules leave the polymer because of the concentration gradient caused by the difference in vapor pressure inside and outside the polymer material.

It can be seen from Fig.3 that the resistance baseline shifts upwards after the second exposure. This can be attributed to a stress relaxation mechanism. During the first exposure, the polymer structure swells. When the sensor is subsequently purged, the polymer chains may relax into a more energetically favorable formation which may be different to that of their initial state. Theoretically, after each exposure the polymer should relax into this more energetically stable state. However, it can be seen that with increasing number of cycles, the recovery period is longer and the polymer never re-attains this energetically favorable configuration.

Fig.4a shows the response of a granular sensor to an acetone vapor, for 5 cycles of purge and exposure. From the temperature of the oil bath, the partial pressure of the acetone vapor was calculated to be 177 mmHg, corresponding to a concentration of 230 000 ppm. Fig 4b shows a single exposure/purge cycle on an expanded time scale.

Typically, the resistance of the sensor doubles upon exposure to the saturated acetone vapor. In the first 4 seconds after exposure, resistance increases from 900 to 2020 Ω , by a factor of around 2.2. During the remaining

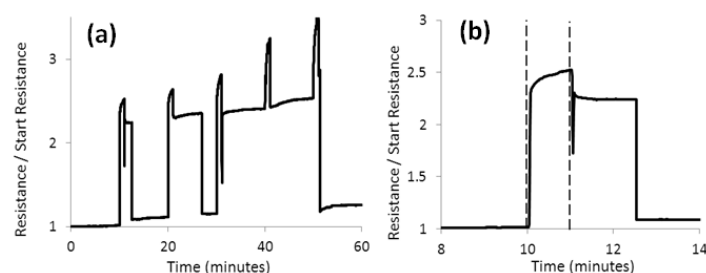


Figure 4. (a) The response of QTCTM granules dispersed in a PVC polymer, after 5 exposures to acetone vapor at a concentration of 230 000 ppm. During exposure, the resistance increases. Recovery after the exposure is much slower than the initial response and the resistance tends towards a baseline much higher than the start resistance. (b) The first exposure is plotted on an expanded time scale. The dashed lines indicate the exposure period.

exposure time, the resistance steadily increases. After the onset of the purge, resistance initially drops by a factor of around 0.1 in the first 5 seconds of the purge. A relaxation process is observed for the next 1 ½ minutes, after which the resistance is observed to rapidly drop back to the start value.

The granular sensors exhibit a larger response to the THF than to the acetone vapor. Despite having a larger vapor concentration, the acetone produces a smaller resistance response. If it were the vapor concentration which was solely responsible for this, one would expect the acetone to produce a larger response as the vapor concentration was higher in this case.

As mentioned previously, solubility parameters play an important role and can be used to assess the compatibility of a solvent/polymer system using (1). Table I shows the solubility parameters of THF, acetone and the PVC polymer matrix, where the last column assesses (1) for both the THF/PVC or acetone/ PVC systems. It can be seen that the differences for each system are in this case identical, predicting an equal magnitude of response. However, it should be noted that (1) gives a very simplistic approach in assessing the solubility match. In reality, it is expected the responses will differ in each case, as acetone has the higher solubility parameter and is therefore more polar than THF. Graham et al investigated granules mixed with a polystyrene based polymer matrix [4]. A greater response was observed using THF vapor than for acetone, as is also observed here for the PVC polymer. However, the solubility parameter for the polystyrene-based polymer is not reported so it is difficult to draw comparisons.

Fig.4 also shows that the resistance response is unstable, in that the resistance transitions rapidly from a high to low value midway during the purge regime, when there appears to be no obvious external cause. A possible reason for this is due to damage to the sensor through prolonged exposure to high concentrations of vapor. Sufficient swelling may lift the sensor from the electrical contacts, producing an apparent instability in the electrical response. Visual inspection showed that there was some damage to the electrical contacts, after prolonged exposures to high vapor concentrations.

Future work may test the response to acetone at lower concentrates, in order to clarify exactly what is causing the anomalies reported above. A wider range of test vapors may be investigated, in order to fully investigate the effect of matching the solubility parameters.

TABLE I. SOLUBILITY PARAMETERS

Solubility Parameter δ (cal/cm ³) ^{1/2} ^a		
Material	δ (cal/cm ³) ^{1/2}	$\sqrt{ \delta - \delta_p }$
Acetone	9.9	0.63
THF	9.1	0.63
PVC	9.5	-

a. Values are converted from those given in Reference: Polymer Properties, a technical document produced by Sigma Aldrich. Available at website url: http://www.sigmaaldrich.com/etc/medialib/docs/Aldrich/General_Information/polymer_solutions.Par.001.File.tmp/polymer_solutions.pdf (Accessed on 28/02/2013)

V. CONCLUSIONS

The utilization of a QTCTM granules produced by Peratech Ltd, in order to detect volatile organic compounds, is of much interest due to the potential applications in artificial olfaction. Similar to other conductive polymer

composites, comprising an electrically conductive filler particle embedded in a polymer matrix, QTCTM granules exhibit an increase in resistance upon exposure to organic vapors. However, the resistance of these granules may increase by over 8 orders of magnitude in a time of typically a few seconds, which offers a vast improvement over other polymer composites where the response is smaller and over a longer period of time. QTCTM materials have been shown to undergo assisted quantum tunneling, rather than direct percolative conduction, and this is responsible for the large responses seen. The granular sensors have been tested with high concentrations of THF and acetone vapors, where THF produces the larger response. This response can be explained by case II diffusion of the vapor into the polymer matrix, such that the matrix swells and decreases the physical pressure on the granules. Solubility parameters provide a method of matching the vapor to the polymer matrix in order to maximize the sensor response. Having established the responses shown in this investigation, further experiments testing a wider range of organic vapors may prove useful, in order to fully characterize the effect of matching the solubility parameter of the analyte to that of the polymer.

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